CHARACTERISTICS OF SYNTHETIC CRUDE FROM CRUDE SHALE OIL PRODUCED BY IN SITU COMBUSTION RETORTING

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INTRODUCTION

The nitrogen contents of in situ crude shale oils may be somewhat lower than those of crude shale oils produced in other retorts;[1] however, these in situ oils still contain more than twice as much nitrogen as high-nitrogen petroleum crude oils. Because existing refineries would not be able to cope with the high nitrogen content of shale oil if it were a substantial portion of the refinery feed, the National Petroleum Council (NPC) has suggested[2] that crude shale oil be upgraded at the retorting site by a catalytic hydrogenation process to produce a synthetic, premium feedstock called "syncrude." The production of such a syncrude from in situ crude shale, a description of its bulk properties, and a comparison of its properties to those of an NPC-type syncrude have been covered by C. M. Frost[3] earlier in this symposium.

This paper reports the compound-type characteristics of the syncrude produced by catalytic hydrogenation of in situ crude oil. Special attention will be devoted to the nitrogen-compound types that are in a syncrude because it will be these compounds with which a refiner will have to deal if he uses this or a similar syncrude as his refinery feed.

In addition to reporting the nitrogen-compound types present in the syncrude, this paper will also report on the nitrogen types in intermediate hydrogenation products in order to relate this study to other studies[4,5,6,7,8] which have shown that the efficacy of nitrogen removal depends upon the nitrogen types in the charge stock. Earlier studies have been on pure compounds, or on charge stocks spiked with pure compounds, or on nitrogen-containing stocks and have been concerned with nitrogen removals approaching 80 percent. The syncrude described in the present work represents a case approaching 95 to 99 percent nitrogen removal.

EXPERIMENTAL

Preparation of the Samples

The synthetic crude oil (syncrude)[3] used in this study was prepared by hydrogenating the naphtha (IBP-350° F), the light oil (350°-550° F), and the heavy oil (550°-850° F) fractions that had previously been obtained from in situ crude shale oil by distillation and coking of the vacuum residuum. The heavy oil used in this study was the 550° F+ material from the heavy-oil hydrogenation. The light oil was the 350° F+ material from the hydrogenation of the light oil from the distillation step combined with the 350°-550° F material from the heavy-oil hydrogenation. The 175°-350° F heavy naphtha was the 175° F+ material from the hydrogenation of the combined IBP-350° F naphtha from the distillation and the heavy naphthas from both the heavy-oil and the light-oil hydrogenations. The C_5-175° F light naphtha was the material with that boiling range from each of the three hydrogenations.

In addition to using these four fractions in the characterization of the syncrude, the nitrogen compounds in three intermediate hydrogenation fractions were characterized in order to relate this denitrification study to other such studies. These materials were the light oil from the

heavy-oil hydrogenation, the 175°-350° F heavy naphtha from the heavy-oil hydrogenation, and the 175°-350° F heavy naphtha from the light-oil hydrogenation.

The heavy oil, which contained nearly 90 percent of the nitrogen in the syncrude, was fractionated by liquid displacement chromatography on Florisil. The nonpolar, nonnitrogen-containing hydrocarbons were washed from the Florisil column with n-heptane; a very weak-base concentrate was displaced with benzene; and a weak-base concentrate was displaced with benzene-methanol azeotrope.

Analytical Methods

Total nitrogen values were determined with a reductive, hydrogen-nickel pyrolysis tube and an ammonia microcoulometer. Nonaqueous potentiometric titration[6,9,10,11] was used to classify the nitrogen compounds into weak-base (pKa -2 to +2), very weak-base (pKa +2 to +8), and neutral types. Infrared spectrometry[10,11,12] was used to determine the concentration of pyrrolic nitrogen (nonhydrogen-bonded N-H). Colorimetry[10,13,14] was used to determine pyrroles and indoles with unsubstituted α or β positions. The aforementioned methods classified the nitrogen compounds into weak bases such as pyridines (including quinolines, 5,6,7,8-tetrahydroquinolines and acridines) and as arylamines (including 1,2,3,4-tetrahydroquinolines, 2,3-dihydroindoles, and anilines); into very weak-base pyrroles and indoles with an α or β position unsubstituted; and into neutral carbazoles without N-substitution. Low-voltage mass spectrometry and high-resolution mass spectrometry allowed classification of the remaining nitrogen compounds into either pyrrole types with α and β positions substituted or carbazoles with N-substitution.

Hydrocarbon types were estimated using the subtractive method of Poulson[15,16] for the fractions boiling above 175° F. The hydrocarbon compound composition of the C_5-175° F naphtha was determined by gas chromatography. Paraffin and naphthene contents of the 175°-350° F naphtha and of the 350°-550° F light oil were calculated from mass spectra. Liquid displacement chromatography on Florisil was used to determine the amount of polar material in the 550°-850° F heavy oil.

RESULTS AND DISCUSSION

Hydrocarbon-Type Characterization

Table I lists the four fractions, their weight percent of the syncrude, and their hydrocarbon-type compositions. The values for polar material for the two naphthas and the light oil are estimates based on their nitrogen contents. The polar material value for the heavy oil is based on the recovered weights from the Florisil separation. As shown in Table I, all fractions of the syncrude have appreciable amounts of aromatics after the hydrogenation even though the nitrogen has been largely removed. Only the heavy oil has a detectable concentration of olefinic hydrocarbons. A reference to this olefinic nature will be made later in this paper.

Nitrogen-Type Characterization

Syncrude Fractions.--Table II lists the microcoulometric and titration data for the four syncrude fractions. The 79 ppm nitrogen in the light oil was shown to be all pyridine-type nitrogen because it did not acetylate when acetic anhydride was used as the titration solvent. No further characterization of this nitrogen was carried out. No acetylatable arylamines were found in this fraction or in the heavy oil, although Brown[7] found that anilines made up nearly one-third of the tar-base concentrate from a recycle, hydrocracked shale-oil naphtha (total nitrogen in the naphtha was approximately 1,000 ppm). In addition, Silver[5] reports that in denitrification of

TABLE I. - Hydrocarbon types in syncrude fractions

Boiling range	Name	Wt pct of crude	Hydrocarbon type, wt pct of fraction				
			Paraffins	Naphthenes	Olefins	Aromatics	Polar material
C_5-175° F	Light naphtha	3	71.8	20.5	0.0	7.7	<0.001
175°-350° F	Heavy naphtha	21	42.8	43.4	.0	13.8	< .001
350°-550° F	Light oil	49	1/ 51.5	25.0	.0	23.5	< .01
555°-850° F	Heavy oil	27	1/ 72.7		6.0	19.2	2.1

1/ Includes naphthenes.

TABLE II. - Microcoulometric and titration data for syncrude fractions

Fraction	Total nitrogen in fraction, ppm	Nitrogen type, wt pct of nitrogen in fraction			
		Weak-base	Very weak-base	Neutral	Arylamine
Light naphtha	<0.5	-	-	-	-
Heavy naphtha	.8	-	-	-	-
Light oil	79	100	0	0	0
Heavy oil	935	40.1	13.9	46.0	0

shale gas oil, to about 80 percent removal of nitrogen, arylamines appear to build up relative to the other nitrogen types in the total product oil.

Nitrogen Concentrates.--Table III lists the recovery of the heavy-oil nitrogen in the two Florisil concentrates and also the concentration of nitrogen types in each of these two concentrates. The weak-base and very weak-base types are determined by nonaqueous potentiometric titration, the neutral types by difference, the N-H types by infrared spectrometry, and the pyrrolic types by colorimetry. As shown in Table III, the concentrate labeled very weak base has about one-fifth very weak-base and four-fifths neutral nitrogen compounds, and the nitrogen in the concentrate labeled weak base is nearly all weak-base nitrogen with less than 3 percent being neutral nitrogen.

TABLE III. - Nitrogen distribution in heavy-oil concentrates displaced from Florisil

Concentrate	Recovery, wt pct of nitrogen in the heavy oil	Nitrogen type, wt pct of nitrogen in concentrate				
		N-H	Pyrrolic	Weak-base	Very weak-base	Neutral
Very weak-base concentrate	61.5	63.4	6.8	0.0	19.8	80.2
Weak-base concentrate	38.4	2.3	<0.01	97.4	.0	2.6

Very Weak-Base Nitrogen Concentrate.--Table IV is a summary of the data obtained from low-voltage mass spectrometry and from high-resolution mass spectrometry on the very weak-base concentrate from the Florisil separation. The absence of any titratable weak bases (Table III) allows an assignment of very weak-base or of neutral nitrogen types to the Z series ions as shown in Table IV. The names of the very weak-base nitrogen compounds reflect only the degree of hydrogen deficiency necessary to yield the proper Z series. The requirements for the proper Z series

TABLE IV. - Mass spectral data for very weak-base concentrate

Z series	Compound type	Percent of ionization
- 5	Cycloalkanopyrroles	<1
- 7	Dicycloalkanopyrroles	6
- 9	Indoles	7
-11	Cycloalkanoindoles	3
-13	Dicycloalkanoindoles	13
-15	Carbazoles	54
-17	Cycloalkanocarbazoles	17
-19	Dicycloalkanocarbazoles	<1

could be met by having olefinic bonds in either the cycloalkano rings or in an alkyl substituent on the ring system. For example, the Z = -13 labeled as dicycloolkanoindoles could also be correctly labeled as monocycloalkenoindoles. The inclusion of an olefinic bond in the molecule is reasonable when one considers that 6 percent of the heavy oil hydrocarbon molecules are olefinic (Table I).

Interpretation of these mass-spectral data in Table IV combined with the titration data from Table III allows additional inference concerning the characteristics of the nitrogen compounds present in the very weak-base concentrate. The sum of the compound types listed as pyrroles and indoles (Z = -7, -9, -11, and -13) amounts to 29 percent of the total. These compound types have been shown[11] to give very weak-base titers of about 70 percent of theoretical; thus it appears likely that the 19.8 percent titer for very weak bases in Table III may come from the titration of the pyrroles and indoles in this concentrate. In addition, they are not N-substituted because N-substituted pyrrole-type nitrogen titrates as weak-base nitrogen, and there is no weak-base titer for this concentrate.

A further characterization of these pyrrole-type nitrogen compounds in the very weak-base concentrate can be made by using the colorometric pyrrolic nitrogen value of 6.8 percent (Table III) as the value for α,β-unsubstituted pyrrole-type compounds. This leaves 22.2 percent of the nitrogen in pyrroles and indoles which have both α- and β-substitution. The α,β-unsubstituted pyrroles and indoles also have no N-substitution because these N-substituted compounds would titrate as weak bases and not as very weak bases. This finding of no N-substitution on the pyrroles and indoles is consistent with the research of Jacobson[18,19] who reported that N-alkylpyrroles and N-alkylindoles thermally and irreversibly isomerize to give the α and β alkyl isomers and therefore would not likely be present in crude shale oil.

Table III shows that 63.4 percent of the nitrogen in the very weak-base concentrate is N-H nitrogen. Of this 63.4 percent of the nitrogen, 29 percent has already been characterized as being in pyrroles and indoles without N-substitution. This leaves 34.4 percent of the nitrogen to be in carbazoles without N-substitution. Table IV shows that 71 percent of the nitrogen is in carbazole-type compounds, and if 34.4 percent has no N-substitution then 36.6 percent has N-substitution. Table V is a summary of these findings. Thus we see that one-third of this concentrate is one- and two-aromatic-ring heterocyclics and two-thirds is three-aromatic-ring heterocyclics.

Weak-Base Nitrogen Concentrate.--Table VI is a summary of the mass spectral data on the weak-base concentrate. As was true for the very weak-base fraction, the compound types

TABLE V. - Summary of nitrogen types in the very weak-base nitrogen concentrate

Nitrogen-type compounds	Percent of fraction
Pyrroles or indoles with either α or β positions unsubstituted; no N-substitutions	6.8
Pyrroles or indoles with substitutions in both α and β positions; no N-substitutions	22.2
Carbazoles with no N-substitution	34.4
Carbazoles with N-substitution	36.6

TABLE VI. - Mass spectral data for weak-base concentrate

Z series	Compound type	Percent of ionization
- 5	Pyridines	35
- 7	Cycloalkanopyridines	25
- 9	Dicycloalkanopyridines	12
-11	Quinolines	13
-13	Cycloalkanoquinolines	8
-15	Dicycloalkanoquinolines	3
-17	Acridines	4
-19	Cycloalkanoacridines	<1

reflect only the degree of hydrogen deficiency necessary to achieve the proper Z series; and, like Table IV, this hydrogen deficiency could be achieved by olefinic bonds in the molecule. We can see from Table III that nearly all (97.4 percent) of the nitrogen in this concentrate titrates as weak-base nitrogen; hence the compound types listed in Table VI are generally consistent with that titration. However, Table III does show that 2.3 percent of the nitrogen in this fraction exhibits an N-H character. Because there is no weak-base titer, it can be assumed that this N-H character is in carbazoles either in the Z = -15 or -17 series. This indicates that there was some tailing of the carbazoles into the weak-base fraction. Contrasted to the ring structures in the very weak-base fraction in which one-ring and two-ring structures accounted for only one-third of the fraction and three-ring structures two-thirds, the weak bases are composed of two-thirds one-aromatic-ring structures and one-third two-ring and three-ring structures. Dinneen[20] also showed this preponderance of one-ring materials in a shale-oil gas oil as did Poulson[10] in a shale-oil light distillate.

Characterization of Intermediate Fractions.--Nonaqueous potentiometric titration was used to characterize the nitrogen compounds in three, intermediate fractions from the production of the syncrude. Table VII lists these three fractions, their source, and the results of the titrations. Also listed in this table are the syncrude fractions produced during the hydrogenation.

The first fraction listed is the 550° F+ heavy oil produced by hydrogenation of the 550°-850° F heavy oil from distillation and coking of the in situ crude oil. This is the same fraction listed in Tables I and II as the syncrude heavy oil fraction. The second fraction listed in Table VII is the 350°-550° F light oil produced in the foregoing hydrogenation and the third fraction is the 175°-350° F heavy naphtha produced in the same hydrogenation.

TABLE VII. - Microcoulometer and titration data for selected, intermediate and syncrude fractions

Fraction	Total nitrogen in fraction, ppm	Nitrogen type, wt pct of nitrogen in fraction			
		Weak-base	Very weak-base	Neutral	Arylamine
Heavy-oil hydrogenation					
Heavy oil	935	40.1	13.9	46.0	0
Light oil	1,220	78.7	11.5	9.8	1/ 12.3
Heavy naphtha	299	100.0	0	0	0
Light-oil hydrogenation					
Light oil	79	100.0	0	0	0
Heavy naphtha	53	100.0	0	0	0

1/ Included in weak-base nitrogen.

The fourth fraction in Table VII is the 350°-550° F light oil produced from the hydrogenation of the 350°-550° F light oil resulting from the distillation and coking of the in situ crude to which had been added an aliquot amount of the light oil shown as the second fraction in Table VII. The fifth fraction is the 175°-350° F heavy naphtha from this hydrogenation. Only the second, third, and fifth listed fractions are intermediate fractions; the first and fourth are final, syncrude ones.

There are three purposes in showing the data in Table VII. First, it is evident that when a shale-oil stock is hydrocracked to lower boiling material, the nitrogen content of the lower boiling fraction is higher than when that same boiling-range material is hydrogenated; for example, the light oil from the heavy-oil hydrogenation has 1,220 ppm nitrogen whereas the light oil from the light-oil hydrogenation is only 79 ppm nitrogen. Second, the light oil from the light-oil hydrogenation and both of the naphthas have only weak-base nitrogen, and this is all pyridine type because none of these fractions contains acetylatable amines. And, third, the light oil from the heavy-oil hydrogenation has arylamine-type weak bases, neutral nitrogen compounds, and very weak bases as well as pyridine-type weak bases. These data indicate that an unspecified but appreciable amount of hydrocracking can and does precede denitrification reactions. In general, arylamines are not found in appreciable concentrations in shale-oil distillates, but are presumed to be produced by hydrogenation of a five-membered nitrogen ring to give a 2,3-dihydroindole-type arylamine and by hydrogenation of a six-membered nitrogen ring to give a 1,2,3,4-tetrahydroquinoline-type arylamine.[4,5,6,10] Cracking of this saturated, nitrogen-containing ring with the nitrogen remaining attached to the aromatic moiety results in an aniline-type arylamine. The presence of arylamines in the light-oil fraction from the heavy-oil hydrogenation is consistent with Silver's[5] finding them in the total product from shale gas oil hydrogenation at nitrogen removals approaching the 80-percent level. The fact that the arylamines are not in either of the naphtha materials shown in Table VII nor in the naphthas shown in Table II indicates that arylamines are converted to hydrocarbons and ammonia when nitrogen conversion approaches 95 percent.

SUMMARY

The synthetic crude was produced by hydrogenating the IBP-350° F naphtha, the 350°-550° F light-oil, and the 550°-850° F heavy-oil fractions obtained from in situ crude shale oil by distillation followed by coking of the 850° F+ residuum. Characterization of the syncrude was

accomplished by examining the following fractions: (1) C_5-175° F light naphtha, (2) 175°-350° F heavy naphtha, (3) 350°-550° F light oil, and (4) 550°-850° F heavy oil.

The light naphtha comprised 3 percent of the syncrude and contained 72 percent paraffins, 20 percent naphthenes, 8 percent aromatics, and less than 0.5 ppm nitrogen. The heavy naphtha comprised 21 percent of the syncrude and contained 43 percent paraffins, 43 percent naphthenes, 14 percent aramatics, and less than 1 ppm nitrogen. The light oil comprised 49 percent of the syncrude and contained 51 percent paraffins, 25 percent naphthenes, 24 percent aromatics, and 79 ppm nitrogen. The heavy oil comprised 27 percent of the syncrude and contained 73 percent saturates, 6 percent olefins, 19 percent aromatics, 2 percent polar compounds, and 935 ppm nitrogen.

The nitrogen compounds in the two naphthas were not characterized. The nitrogen in the light oil was shown to be pyridine-type nitrogen with no detectable arylamine-type nitrogen.

The nitrogen compounds in the heavy oil were shown to be 40 percent weak-base, 14 percent very weak-base, and 46 percent neutral compounds. Mass spectrometry was used to classify the weak bases as 72 percent pyridines (one aromatic ring), 24 percent quinolines (two aromatic rings), and 4 percent acridines (three aromatic rings). Mass spectrometry combined with infrared analysis and pyrrolic-nitrogen determination were used to classify the very weak-base and neutral nitrogen compounds as 7 percent pyrroles or indoles with either or both of the α and β positions open and not N-substituted; 22 percent pyrroles or indoles with substitution on both α and β positions but no N-substitutions; 34 percent carbazoles with no N-substitutions; and 37 percent N-substituted carbazoles.

In addition to characterizing the four fractions of the final syncrude product, three intermediate fractions were also characterized. The heavy naphtha from the light-oil hydrogenation and the heavy naphtha from the heavy-oil hydrogenation both contained characterizable amounts of nitrogen compounds. These were shown to be weak bases of the pyridine type. The light oil from the heavy-oil hydrogenation had the greatest concentration of nitrogen of any of the fractions examined, 1,220 ppm. Nonaqueous titration showed these nitrogen compounds to be 66 percent weak-base pyridines, 12 percent weak-base anilines (arylamines), 12 percent very weak bases, and 10 percent neutral compounds. This material contained the only evidence of arylamines in the product from these hydrogenations, which represent removals of 95 to 99.9 percent of the nitrogen of the charge stock.

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Reference to specific trade names or manufacturers does not imply endorsement by the Bureau of Mines.

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